

Influence of an annealing ambient in post-annealing process of LiCoO₂ cathodes for rechargeable thin film batteries

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Crystalline LiCoO₂ has been widely used as the cathode material in secondary rechargeable lithium batteries[1]. Almost most crystalline cathode films for the thin film batteries have been grown by the sputtering system followed by post-annealing process[2]. However, the effects of annealing ambient of LiCoO₂ cathode during the post-annealing process for rechargeable thin film batteries have not been systematically researched so far. We systematically investigate the effects of annealing ambient during post-annealing process on LiCoO₂ cathode films grown by the sputtering system.

The films grown by RF sputtering system were annealed for 30 min at 650, 750, 800, 850, and 900 °C under Ar or O₂ ambient of 10 mtorr, respectively. Li foil and LiCoO₂ film were used as anode and cathode, respectively. The electrolyte was 1 M LiCF₃SO₃ dissolved in PC+DME (1:2) and all the cells were prepared in a dry room.

Figure 1 shows the discharge curves with current rate for the LiCoO₂ films annealed 750 and 850 °C, respectively, under Ar (a,b) and O₂ (c,d) ambient. Figure 1(a) and (c) show smooth discharge curves without any plateau, indicating that the LiCoO₂ films annealed at 750 °C have amorphous structure. In contrast, fig. 1(b) and (d) show typical discharge curves of crystalline LiCoO₂ films, which have the plateaus at 3.93, 4.07, and 4.17 V indicating phase transformation. Figure 1 also shows that crystalline LiCoO₂ films have better rate performance than amorphous LiCoO₂ films. The LiCoO₂ films annealed at 800 °C showed medium shape between the discharge curves of crystalline and amorphous LiCoO₂ films (not shown here), indicating uncompleted crystallization of the

LiCoO₂ film. X-ray diffraction data confirmed it. The surface roughness measured by atomic force microscopy (AFM) was rapidly increased at 800 °C.

Figure 2 shows the discharge capacity retention (R_{40/1}), ratio of 1 to 40 cycle number, with an annealing temperature. The LiCoO₂ film annealed at 900 °C under Ar ambient was cycled to 10 times.

From above results, post-annealing process under O₂ ambient can accomplish superior long-term cycling performance and thermal stability above 800 °C, compared with that under Ar inert ambient. It may be due to the cathode degradation caused by oxygen out-diffusion from LiCoO₂ films annealed at high temperature under Ar inert ambient. Surface roughening above 800 °C increased the initial specific capacity but caused worse long-term cycling performance.

References

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[2] B.Wang, J.B.Bates, F.X.Hart, B.C.Sales, R.A.Zuhr, and D.Robertson, J. Electrochem. Soc. **143**, 3203 (1996).

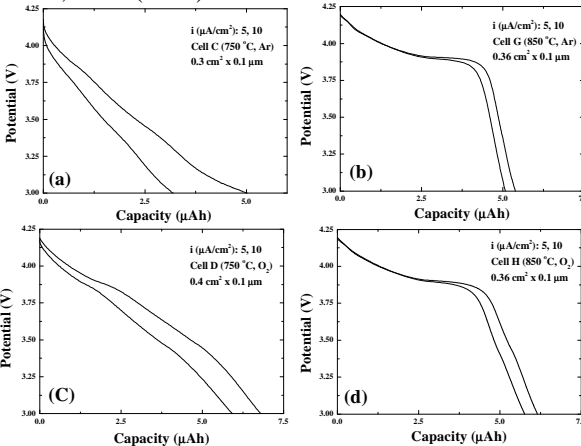


Figure 1. Discharge curves with current rates for LiCoO₂ films annealed at 750 and 850 °C, respectively, under Ar (a,b) and O₂ (c,d) ambient.

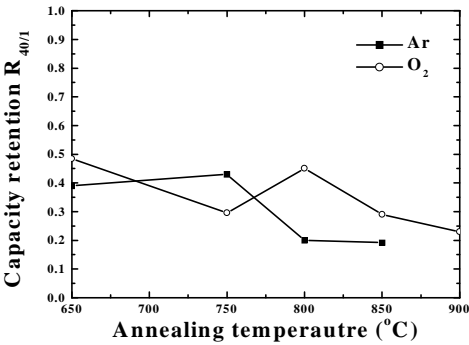


Figure 2. Discharge capacity retention (R_{40/1}) for the LiCoO₂ films with the annealing temperature.